

VERIFICATION OF TRANSLATION

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translation of the Japanese Patent Application No. Hei 10-207329
in the name of KANEKA CORPORATION.

Dated this *6th* day of *August*, 2004



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[Document Name] Patent Application

[Filing Number] KEN-3546

[Filing Date] July 23, Heisei 10

[To] Commissioner, Patent Office

[IPC] C08F 20/18

[Title of the Invention] POLYMER AND USE

[Number of Claims] 20

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[Indication of Fee]

[Number of Deposit Ledger] 005027

[The Amount of Payment] 21,000 yen

[List of Attached Documents]

[Document Name] Description 1

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[Document Name]
[Necessity of Proof]

Abstract
Needed

1

[Document Name] Description

[Title of the Invention] POLYMER AND USE

[Scope of Claims for Patent]

[Claim 1] A block copolymer which is produced by adding a
5 polymer (I) produced by living cationic polymerization and
containing a group represented by the general formula 1:



(wherein R^1 represents a hydrogen atom or a hydrocarbon group
containing 1 to 20 carbon atoms) in at least one terminus to
10 a living radical polymerization system.

[Claim 2] The polymer according to Claim 1, wherein, in the
general formula 1, R^1 is a hydrogen atom.

[Claim 3] The polymer according to Claim 1 or 2, wherein the
polymer (I) is a styrenic polymer.

15 [Claim 4] The polymer according to Claim 1 or 2, wherein the
polymer (I) is an isobutylene polymer.

[Claim 5] The polymer according to Claim 1 or 2, wherein the
polymer (I) is a polyether polymer.

[Claim 6] The polymer according to Claim 1 or 2, wherein the
20 polymer (I) is a vinyl ether polymer.

[Claim 7] The polymer according to any of Claims 1 to 6,
wherein the polymer (I) has a glass transition point not higher
than 25°C.

[Claim 8] The polymer according to any of Claims 1 to 7,
25 wherein the polymer (I) has a plurality of the groups
represented by the general formula 1.

[Claim 9] The polymer according to any of Claims 1 to 8,
wherein the polymer (I) has the number average molecular weight
of 500 to 100000.

30 [Claim 10] The polymer according to any of Claims 1 to 9,
wherein the polymer (I) has the ratio between the weight average
molecular weight (M_w) and the number average molecular weight
(M_n) (M_w/M_n) as determined by gel permeation chromatography of
less than 1.8.

35 [Claim 11] The polymer according to any of Claims 1 to 10,

wherein a polymer chain produced by living radical polymerization comprising adding the polymer (I) has a glass transition point not higher than 25°C.

5 [Claim 12] The polymer according to any of Claims 1 to 10, wherein a polymer produced by living radical polymerization comprising adding the polymer (I) is a styrenic polymer.

[Claim 13] The polymer according to any of Claims 1 to 10, wherein a polymer produced by living radical polymerization comprising adding the polymer (I) is a (meth)acrylic polymer.

10 [Claim 14] The polymer according to any of Claims 1 to 13, wherein the living radical polymerization comprising adding the polymer (I) is a polymerization system comprising polymerizing a vinyl monomer using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of
15 the group 7, 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst.

[Claim 15] The polymer according to Claim 14, wherein the metal complex to serve as a catalyst for the living radical polymerization comprising adding the polymer (I) is a copper,
20 nickel, ruthenium or iron complex.

[Claim 16] The polymer according to Claim 15, wherein the metal complex to serve as a catalyst for the living radical polymerization comprising adding the polymer (I) is a copper complex.

25 [Claim 17] The polymer according to Claims 1 to 16, wherein the living radical polymerization comprising adding the polymer (I) is started by a di- or more functional initiator.

[Claim 18] The polymer according to any of Claims 1 to 17, wherein the ratio between the weight average molecular weight (Mw) and the number average molecular weight (Mn) (Mw/Mn) as
30 determined by gel permeation chromatography of not more than 1.8.

[Claim 19] A thermoplastic elastomer which comprises, as the main component thereof, the polymer according to any of Claims
35 1 to 18.

[Claim 20] An impact resistance improving agent which comprises, as the main component thereof, the polymer according to any of Claims 1 to 18.

[Detailed Description of the Invention]

5 [0001]

[Technical Field of the Invention]

The present invention relates to a method for producing a block copolymer which comprises adding an alkenyl-terminated polymer produced by living cationic polymerization to a living
10 radical polymerization system, the polymer, and its use.

[0002]

[Prior Art]

Block copolymers composed of different polymer block species bound to each other are generally produced by
15 polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block copolymers using them. When cationic polymerization is employed, however, it is difficult to control the
20 polymerization, since the growing species carbenium ion is unstable. In recent years, examples of the so-called living cation polymerization in which the growing carbenium ion in the cationic polymerization is inhibited from undergoing isomerization, chain transfer reaction or termination reaction
25 have been reported. For example, Higashimura et al. (Macromolecules, 17, 265, 1984) report that cationic living polymerization is possible in vinyl ether polymerization using a combination of hydrogen iodide and iodine as an initiator. However, the polymerization using such initiator has various
30 problems; for instance, its application is restricted to those monomers which have an alkoxy group high in electron donating ability and are highly susceptible to cationic polymerization, and the initiator is unstable and difficult to handle.

[0003]

35 On the other hand, Kennedy et al. (Japanese Kokai

Publication Sho-62-48704, Japanese Kokai Publication Sho-64-62308), by polymerizing olefin monomers, such as isobutylene, using an organic carboxylic acid or an ester, or an ether as an initiator in combination with a Lewis acid, showed
5 that cationic living polymerization is possible with olefin monomers as well. This method has been modified in several ways, and Nippon Zeon (Japanese Kokoku Publication Hei-07-59601) has succeeded in obtaining block copolymers by successive monomer addition with additional use of an amine. In this modification,
10 isobutylene-based block copolymers comprising an isobutylene polymer and a styrene polymer are produced in an mixed solvent composed of methylene chloride and hexane. However, such halogenated hydrocarbons containing 1 or 2 carbon atoms have problems; for instance, they are difficult to handle, and
15 require large scale equipment for preventing them from being discharged into the environment to raise the cost of production. Although, on the other hand, such polymerization is also possible in a halogen-free solvent such as toluene, very fine adjustment is required, depending on the monomer, for the
20 monomer to show adequate polarity. It is thus very difficult to establish the conditions for successive polymerization of two or more monomer species differing in reactivity.
[0004]

Meanwhile, in recent years, controlled radical
25 polymerization techniques and, further, living radical polymerization techniques have been developed, making it possible to well control the living polymerization. Matyjaszewski et al. report a method of synthesizing block copolymers by successively adding monomers using the atom
30 transfer radical polymerization technique to be mentioned later herein or by using a macro-initiator. These techniques, however, may sometimes encounter problems; successive polymerization of monomers is difficult since respective monomers require different optimum polymerization conditions,
35 or it is difficult to introduce, terminally into the

macro-initiator, an initiator terminus optimal to the next monomer to be polymerized.

[0005]

[Subject which the Invention is to Solve]

5 The present invention has for its object to provide a method for easily producing a block copolymer composed of any of various living cationic polymerization polymers and a living radical polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

10 [0006]

[Means for Solving the Problems]

The present invention relates to a block copolymer which is produced by adding a polymer (I) produced by living cationic polymerization and containing a group represented by the

15 general formula 1:



(wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) in at least one terminus to a living radical polymerization system.

20 [0007]

The polymer block copolymer and the respective polymer blocks of the present invention also have a characteristic for having a narrow molecular weight distribution.

25 The main chain of the polymer (I) is not particularly restricted, but is preferably an isobutylene polymer, styrene polymer, polyether polymer, and vinyl ether polymer.

[0008]

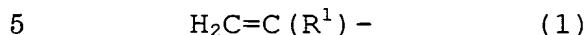
30 The living radical polymerization system to which the polymer (I) is added is not particularly restricted, but is preferably an atom transfer radical polymerization system.

The block copolymer of the present invention is useful as a thermoplastic elastomer or an impact resistance improving agent.

[0009]

35 [Embodiment of the Invention]

The present invention relates to a block copolymer which is produced by adding a polymer (I) produced by living cationic polymerization and containing a group represented by the general formula 1:



in at least one terminus to a living radical polymerization system.

Description of polymer (I)

In the general formula 1, R^1 is a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:

- $(\text{CH}_2)_n-\text{CH}_3$, - $\text{CH}(\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$, - $\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$,
 - $\text{CH}(\text{CH}_2\text{CH}_3)_2$, - $\text{C}(\text{CH}_3)_2-(\text{CH}_2)_n-\text{CH}_3$, - $\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$,
 - C_6H_5 , - $\text{C}_6\text{H}_5(\text{CH}_3)$, - $\text{C}_6\text{H}_5(\text{CH}_3)_2$, - $(\text{CH}_2)_n-\text{C}_6\text{H}_5$, - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)$,
 - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)_2$

(wherein n is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

[0010]

The number of the groups represented by the general formula 1 in polymer (I) is not particularly restricted but may be selected depending on the structure of the desired block copolymer. Thus, said polymer may have one, two or more alkenyl groups.

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the polymer (I) of the present invention is not particularly restricted but is preferably less than 1.8, more preferably not more than 1.7, still more preferably not more than 1.6, much more preferably not more than 1.5, in particular not more than 1.4, most preferably not more than 1.3. In the practice of the present invention, the number average molecular weight can be determined by GPC generally using chloroform as mobile phase and a polystyrene gel column and thus it can be expressed in

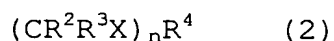
terms of polystyrene equivalent.

[0011]

The number average molecular weight of the vinyl polymer of the present invention is not particularly restricted but is preferably within the range of 500 to 1,000,000, more preferably within the range of 1,000 to 100,000.

<Living cationic polymerization>

In the practice of the present invention, the living cationic polymerization for producing the polymer (I) comprises polymerizing a cationically polymerizable monomer in the presence of a compound of the following general formula 2:



(wherein X is a substituent selected from a halogen atom, an alkoxy group having 1 to 6 carbon atoms and an acyloxy group, R² and R³ may be the same or different and each is a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms, R⁴ is a polyvalent aromatic or aliphatic hydrocarbon group and n is a natural number of 1 to 6).

<Monomer>

The monomer to be used for the living cationic polymerization according to the present invention is not particularly restricted but includes, for example, aliphatic olefins, aromatic vinyls, dienes, vinyl ethers, silanes, vinylcarbazole, β -pinene, acenaphthylene, cyclic ethers and like monomers.

[0012]

As the aliphatic olefin monomers, there may be mentioned isobutylene, ethylene, propylene, 1-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, hexene, cyclohexene, 4-methyl-1-pentene, vinylcyclohexene, octene, norbornene and the like.

As the aromatic vinyl monomers, there may be mentioned styrene, o-, m- or p-methylstyrene, α -methylstyrene, β -methylstyrene, 2,6-dimethylstyrene, 2,4-dimethylstyrene, α -methyl-o-methylstyrene,

α -methyl-m-methylstyrene, α -methyl-p-methylstyrene,
 β -methyl-o-methylstyrene, β -methyl-m-methylstyrene,
 β -methyl-p-methylstyrene, 2,4,6-trimethylstyrene,
 α -methyl-2,6-dimethylstyrene, α -methyl-2,4-dimethylstyrene,
5 β -methyl-2,6-dimethylstyrene, β -methyl-2,4-dimethylstyrene,
o-, m- or p-chlorostyrene, 2,6-dichlorostyrene,
2,4-dichlorostyrene, α -chloro-o-chlorostyrene,
 α -chloro-m-chlorostyrene, α -chloro-p-chlorostyrene,
 β -chloro-o-chlorostyrene, β -chloro-m-chlorostyrene,
10 β -chloro-p-chlorostyrene, 2,4,6-trichlorostyrene,
 α -chloro-2,6-dichlorostyrene, α -chloro-2,4-dichlorostyrene,
 β -chloro-2,6-dichlorostyrene, β -chloro-2,4-dichlorostyrene,
o-, m- or p-t-butylstyrene, o-, m- or p-methoxystyrene,
o-, m- or p-chloromethylstyrene,
15 o-, m- or p-bromomethylstyrene, silyl-substituted styrene
derivatives, indene, vinyl-naphthalene and the like.
[0013]

As the diene monomers, there may be mentioned butadiene,
isoprene, cyclopentadiene, cyclohexadiene, dicyclopentadiene,
20 divinylbenzene, ethylidenenorbornene and the like.

As the vinyl ether monomers, there may be mentioned methyl
vinyl ether, ethyl vinyl ether, (n-, iso)propyl vinyl ether,
(n-, sec-, tert-, iso)butyl vinyl ether, methyl propenyl ether,
ethyl propenyl ether and the like.
25 [0014]

As the silane compounds, there may be mentioned
vinyltrichlorosilane, vinylmethyldichlorosilane,
vinyl-dimethylchlorosilane, vinyl-dimethylmethoxysilane,
vinyltrimethylsilane, divinyl-dichlorosilane,
30 divinyl-dimethoxysilane, divinyl-dimethylsilane,
1,3-divinyl-1,1,3,3-tetramethyldisiloxane,
trivinylmethylsilane, γ -methacryloyloxy-
propyltrimethoxysilane, γ -methacryloyloxypropyl-
methyldimethoxysilane and the like.
35 [0015]

As the cyclic ether, there may be mentioned tetrahydrofuran, which becomes a polyether by polymerization.

These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers, isobutylene
 5 monomers, vinyl ether monomers, and cyclic ether monomers are preferred from the viewpoint of physical properties of the products. More preferred are isobutylene monomers. In the practice of the present invention, such a preferred monomer may be copolymerized with some other monomers and, on that occasion,
 10 the content of such preferred monomer is preferably 40% on the weight basis.

<Initiator>

The above-mentioned compound of the general formula 2 serves as an initiator and forms a carbon cation in the presence
 15 of a Lewis acid and the like, and carbon cation presumably serves as a site of initiation of cationic polymerization. As examples of the compound of the general formula 2 to be used in the present invention, there may be mentioned the following:

[0016]

20 (1-chloro-1-methylethyl)benzene [$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{Cl}$],
 1,4-bis(1-chloro-1-methylethyl)benzene
 [$1,4\text{-Cl}(\text{CH}_3)_2\text{CC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{Cl}$],
 1,3-bis(1-chloro-1-methylethyl)benzene
 [$1,3\text{-Cl}(\text{CH}_3)_2\text{CC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{Cl}$],
 25 1,3,5-tris(1-chloro-1-methylethyl)benzene
 [$1,3,5\text{-(ClC}(\text{CH}_3)_2)_3\text{C}_6\text{H}_3$],
 1,3-bis(1-chloro-1-methylethyl)-(5-tert)-butylbenzene
 [$1,3\text{-(C}(\text{CH}_3)_2\text{Cl)}_2\text{-5-(C}(\text{CH}_3)_3\text{)C}_6\text{H}_3$]

Particularly preferred among them are
 30 bis(1-chloro-1-methylethyl)benzenes [$\text{C}_6\text{H}_4(\text{C}(\text{CH}_3)_2\text{Cl})_2$]
 (bis(1-chloro-1-methylethyl)benzenes are also called bis(α -chloroisopropyl)benzenes, bis(2-chloro-2-propyl)benzenes or dicumyl chlorides). These are bifunctional initiators and, when the polymerization is started with these, polymers having
 35 growing termini at both ends are obtained.

<Catalyst>

The polymerization for producing isobutylene-derived block copolymers may be carried out in the presence of a Lewis acid catalyst. Such Lewis acid may be any of those which can be used in cationic polymerization. Suited for use are, for example, metal halides such as TiCl_4 , TiBr_4 , BCl_3 , BF_3 , $\text{BF}_3 \cdot \text{OEt}_2$, SnCl_4 , SbCl_5 , SbF_5 , WCl_6 , TaCl_5 , VCl_5 , FeCl_3 , ZnBr_2 , AlCl_3 and AlBr_3 ; and organometal halides such as Et_2AlCl and EtAlCl_2 . Considering the catalytic activity and commercial availability, TiCl_4 , BCl_3 and SnCl_4 are preferred. The amount of the Lewis acid to be used is not particularly restricted but can be selected according to the polymerization characteristics or concentration of the monomer employed. Generally, the catalyst is used in an amount of 0.1 to 100 mole equivalents, preferably 1 to 60 mole equivalents, relative to the compound of the general formula 12.

<Electron-donating component>

The polymerization for producing isobutylene-derived block copolymers may also be carried out, when necessary, in the presence of an electron-donating component. Said electron-donating component is considered to have a stabilizing effect on growing carbon cations in cationic polymerization and, upon adding such electron donor, polymers having a controlled structure narrow in molecular weight distribution are formed. The electron-donating component which can be used is not particularly restricted but includes, among others, pyridines, amines, amides, sulfoxides, esters and metal compounds having an oxygen atom bound to the metal atom.

[0017]

The amount of use of each component can adequately be designed according to the characteristics of the desired polymer.

<Polymerization conditions>

The present invention can be carried out in a solvent, if necessary. Any solvent can be used without any particular

limitation provided that it will not substantially inhibit the cationic polymerization. Typically, there may be mentioned halogenated hydrocarbons such as methyl chloride, dichloromethane, chloroform, ethyl chloride, dichloroethane, n-propyl chloride, n-butyl chloride and chlorobenzene; benzene and alkylbenzenes such as toluene, xylene, ethylbenzene, propylbenzene and butylbenzene; straight-chain aliphatic hydrocarbons such as ethane, propane, butane, pentane, hexane, heptane, octane, nonane and decane; branched aliphatic hydrocarbons such as 2-methylpropane, 2-methylbutane, 2,3,3-trimethylpentane and 2,2,5-trimethylhexane; alicyclic hydrocarbons such cyclohexane, methylcyclohexane and ethylcyclohexane; paraffin oils purified from petroleum fractions by hydrogenation; and the like. Among these, toluene-containing mixed solvents are preferred in view of safety to the environment and polymerization physical properties. Primary and/or secondary monohalogenated hydrocarbons containing 3 to 8 carbon atoms are also preferably used. As specific examples of such that can be used are 1-chloropropane, 1-chloro-2-methylpropane, 1-chlorobutane, 1-chloro-2-methylbutane, 1-chloro-3-methylbutane, 1-chloro-2,2-dimethylbutane, 1-chloro-3,3-dimethylbutane, 1-chloro-2,3-dimethylbutane, 1-chloropentane, 1-chloropentane, 1-chloro-2-methylpentane, 1-chloro-3-methylpentane, 1-chloro-4-methylpentane, 1-chlorohexane, 1-chloro-2-methylhexane, 1-chloro-3-methylhexane, 1-chloro-4-methylhexane, 1-chloro-5-methylhexane, 1-chloroheptane, 1-chlorooctane, 2-chloropropane, 2-chlorobutane, 2-chloropentane, 2-chloropentane, 2-chlorohexane, 2-chloroheptane, 2-chlorooctane and chlorobenzene. These may be used singly or two or more of them may be used in combination. Among them, 1-chlorobutane is preferred from the viewpoint of equilibrium among solubility of isobutylene-derived block copolymers, ease of decomposition for rendering the same nonhazardous, cost and

other factors.

[0018]

These solvents are used singly or in combination considering the balance between the polymerization
5 characteristics of the monomers constituting the block copolymer and the solubility of the product polymer, for instance.

The amount of solvent to be used is selected, considering the viscosity of the polymer solution to be obtained and the
10 ease of removal of heat, so that the polymer concentration may be 1 to 50% by weight, preferably 5 to 35% by weight.

[0019]

In practicing the polymerization, the respective components are mixed up with cooling, for example at a
15 temperature of -100°C to not higher than 0°C . A particularly preferred temperature range for attaining a balance between the cost of energy and the stability of polymerization is -30°C to -80°C .

<Terminal functional group introduction>

20 The method of introducing the group represented by the general formula 1 into a terminus of the polymer produced by living cationic polymerization is not particularly restricted but includes the following, for instance:

(1) Method using an allylsilane

25 As disclosed in Japanese Kokai Publication Sho-63-105005, the polymer obtained by the Inifer method for living cationic polymerization is reacted, immediately after polymerization or after formation, with allyltrimethylsilane to give an allyl-terminated polymer.

30 (2) Method using an unconjugated diene

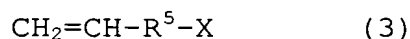
As disclosed in Japanese Kokai Publication Hei-04-288309, an unconjugated diene, such as 1,7-octadiene, is added to an Inifer method living cationic polymerization system to give an allyl-terminated polymer.

35 (3) Method using an organometallic reagent

As disclosed in Japanese Kokai Publication Hei-04-311705, the chlorine atom terminus of a polyisobutylene polymer is alkylated with a Grignard reagent or an alkyllithium. The use of an alkenyl-containing Grignard reagent results in introduction of the alkenyl group.

(4) Method comprising hydroxyl group conversion

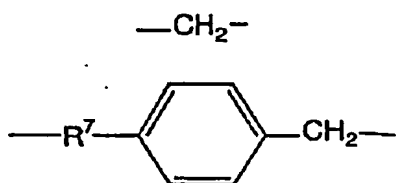
The hydroxyl group at a terminus, in the main chain or in a side chain is converted to -ONa or -OK, for instance, followed by reaction with an organic halide represented by the general formula 3:



[wherein X is a halogen atom such as a chlorine or iodine atom and R^5 is a divalent organic group represented by $-\text{R}^6-$, $-\text{R}^6-\text{OC}(=\text{O})-$ or $-\text{R}^6-\text{C}(=\text{O})-$ (in which R^6 is a divalent hydrocarbon group having 1 to 20 carbon atoms, preferably an alkylene, cycloalkylene, arylene or aralkylene group), more preferably a divalent group selected from the group consisting of $-\text{CH}_2-$ and

[0020]

[Chemical 1]



[0021]

(in which R^7 is a hydrocarbon group having 1 to 10 carbon atoms)], whereby an alkenyl-terminated saturated hydrocarbon polymer is produced.

As the method of converting the terminal hydroxyl group of a hydroxyl-terminated saturated hydrocarbon polymer to an oxymetal group, there may be mentioned the method comprising reacting said polymer with an alkali metal such as Na or K; a metal hydride such as NaH; a metal alkoxide such as NaOCH_3 ; a caustic alkali such as caustic soda or caustic potash or the

like.

[0022]

The above method gives an alkenyl-terminated saturated hydrocarbon polymer having almost the same molecular weight as that of the hydroxyl-terminated saturated hydrocarbon polymer used as starting material. When a polymer with a higher molecular weight is desired, the starting material is reacted with a polyvalent organic halide containing two or more halogen atoms per molecule, for example methylene chloride, bis(chloromethyl)benzene or bis(chloromethyl) ether, prior to the reaction with an organic halide of the general formula 3, whereby the molecular weight can be increased. The subsequent reaction with the organic halide of the general formula 3 can give an alkenyl-terminated hydrogenated polybutadiene polymer with a higher molecular weight.

[0023]

Specific examples of the organic halide represented by the general formula 3 are, but are not limited to, allyl chloride, allyl bromide, vinyl(chloromethyl)benzene, allyl(chloromethyl)benzene, allyl(bromomethyl)benzene, allyl chloromethyl ether, allyl(chloromethoxy)benzene, 1-hexenyl(chloromethoxy)benzene and allyloxy(chloromethyl)benzene. Among these, allyl chloride is preferred in view of its inexpensiveness and ready reactivity.

(5) Method utilizing the Friedel-Crafts reaction

Alkenyl group introduction is realized by subjecting one of various alkenyl phenyl ethers and a Cl group to Friedel-Crafts reaction. And, after hydroxyl group introduction by subjecting one of various phenols and a Cl group to Friedel-Crafts reaction the above-mentioned method for alkenyl group introduction is combinedly applied.

(6) Method comprising an elimination reaction

As disclosed in US Patent 4,316,973, a halogen-terminated polyisobutylene polymer synthesized by the Inifer method for living cationic polymerization is subjected to hydrogen halide

elimination, to thereby effect terminal alkenyl group introduction.

(7) Method utilizing an alkenyl-containing initiator

As disclosed in J. Polym. Sci., Part A: Polym. Chem., 2699
5 (1994).

(8) Method utilizing a silyl enol ether

As disclosed in J. Polym. Sci., Part A: Polym. Chem., 2531
(1994), trimethylsilyl methacrylate is reacted with the living
cationic polymerization terminus to effect introduction of a
10 methacryloyl group.

[0024]

Among these methods, (1) and (2) are preferred.

Production of a block copolymer

In the present invention, a block copolymer is produced
15 by adding the above-mentioned polymer (I) to a living radical
polymerization system.

In the following, the living radical polymerization is
described.

<Living radical polymerization>

20 In its narrow sense, the term "living polymerization"
means that polymerization in which the molecular chain grows
while a terminus always retain activity. Generally, however,
it also includes, within the meaning thereof, pseudoliving
polymerization in which molecules grow while terminally
25 inactivated molecules and terminally activated ones are in
equilibrium. The latter definition is to be applied to the
present invention. "Living radical polymerization" has
recently been aggressively investigated by a number of groups.
As examples, there may be mentioned, among others, the method
30 which uses cobalt porphyrin complex (Journal of the American
Chemical Society, 1994, vol. 116, page 7943), the method which
uses a radical capping agent, for example a nitroxide compound
(Macromolecules, 1994, vol. 27, page 7228), and atom transfer
radical polymerization (ATRP) in which an organic halide, for
35 instance, is used as an initiator and a transition metal complex

as a catalyst. The living radical polymerization hardly undergo termination reaction and give polymers narrow in molecular weight distribution (M_w/M_n being about 1.1 to 1.5) and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization regarded as difficult to control because of a high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other, among others.

10 [0025]

"Living radical polymerization methods", which enable introduction of a specific functional group-containing monomer into a polymer at a substantially arbitrary site thereof in addition to obtaining polymers with a narrow molecular weight distribution and a low viscosity on its properties, are more preferred as methods of producing the specific functional group-containing vinyl polymers.

Among such "living radical polymerization methods", the "atom transfer polymerization methods" for polymerizing vinyl monomers using an organic halide, sulfonyl halide or the like as an initiator and a transition metal complex as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614; Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721) are more preferred as the method of producing specific functional group-containing vinyl polymers, since, in addition to the characteristic features of the above-mentioned "living radical polymerization methods", halogen, etc., relatively favorable for functional group conversion reactions is contained at its terminus and the degree of freedom is high in designing the initiator or catalyst. Also in the method of the present invention, the atom transfer polymerization method is preferred.

35 [0026]

In this atom transfer radical polymerization, an organic halide, in particular an organic halide having a highly reactive carbon-halogen bond (e.g. a carbonyl compound having a halogen in α -position or a compound having a halogen at the benzyl site),
 5 or a sulfonyl halide compound is used as an initiator.

<Monomer>

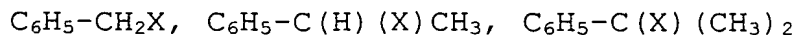
The vinyl monomer used in the living radical polymerization of the present invention is not particularly restricted, and various ones may be used. Examples are
 10 (meth)acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl
 15 (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate,
 20 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl
 25 (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate,
 30 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, α -methylstyrene, chlorostyrene, styrenesulfonic acid and
 35 salts thereof; fluorine-containing vinyl monomers such as

perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing vinyl monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide monomers such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amide group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products. More preferred are acrylic acid ester monomers and methacrylic acid ester monomers, and still more preferred are butyl acrylate monomers. In the practice of the present invention, such a preferred monomer may be copolymerized with some other monomers and, on that occasion, the content of such preferred monomer is preferably 40% on the weight basis. The term (meth)acrylic acid employed hereinabove means acrylic acid and/or methacrylic acid.

[0027]

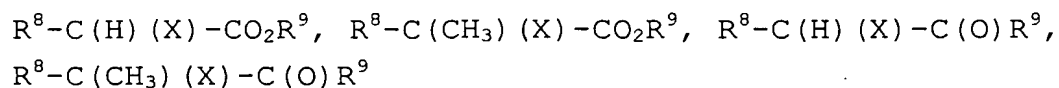
30 <Initiator of atom transfer radical polymerization>

The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, among others:

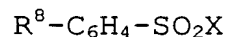


35 (in the above chemical formulas, C_6H_5 is a phenyl group and X

is chlorine, bromine or iodine);



(in which R^8 represents a hydrogen atom or an alkyl group having
5 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or
an aralkyl group having 7 to 20 carbon atoms, X is chlorine,
bromine or iodine, and R^9 represents a monovalent organic group
having 1 to 20 carbon atoms); and



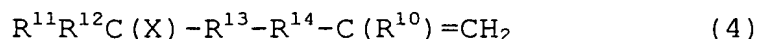
10 (in which R^8 is a hydrogen atom or an alkyl group having 1 to
20 carbon atoms, an aryl group having 6 to 20 carbon atoms or
aralkyl group having 7 to 20 carbon atoms, and X is chlorine,
bromine or iodine).

[0028]

15 Furthermore, when an organic halide or sulfonyl halide
having a functional group other than the functional group for
initiating polymerization is used as the initiator, a polymer
introduced with a functional group at its terminus can be easily
obtained. As such functional group, there may be mentioned
20 alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among
others. By introducing the group represented by the general
formula 1 to the polymer produced from an initiator containing
such functional group by various methods described later to
produce the polymer (I), and adding the polymer to the living
25 radical polymerization system, a block copolymer containing
carious functional group at its terminus can be easily obtained.

[0029]

The alkenyl-containing organic halide is not restricted
but may be one having the structure shown by the general formula
30 4:



(wherein R^{10} is a hydrogen atom or a methyl group, R^{11} and R^{12}
each is a hydrogen atom or a monovalent alkyl having 1 to 20
carbon atoms, an aryl group having 6 to 20 carbon atoms or an
35 aralkyl group and R^{11} and R^{12} may be bound to each other at

respective other termini, R^{13} is $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group, R^{14} is a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally contain one or more ether bonds, and X is
 5 chlorine, bromine or iodine).

In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization is started after the carbon-halogen bond is activated.

[0030]

10 As specific examples of the substituents R^{11} and R^{12} , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc. R^{11} and R^{12} may be bound to each other at respective other termini to form a cyclic skeleton. In such case, $-R^{11}-R^{12}-$ may be, for example, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$,
 15 $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$ and the like.

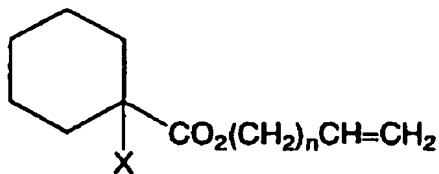
[0031]

As specific examples of the alkenyl-containing organic halide represented by the general formula 4, there may be mentioned the following:

20 $XCH_2C(O)O(CH_2)_nCH=CH_2$,
 $H_3CC(H)(X)C(O)O(CH_2)_nCH=CH_2$,
 $(H_3C)_2C(X)C(O)O(CH_2)_nCH=CH_2$,
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nCH=CH_2$

[0032]

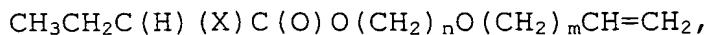
25 [Chemical 2]



30 [0033]

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

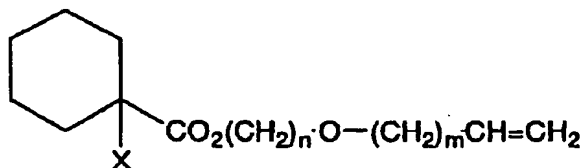
$XCH_2C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,
 $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,
 35 $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$,



[0034]

[Chemical 3]

5



[0035]

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

10 o, m, p-XCH₂-C₆H₄-(CH₂)_n-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)_n-CH=CH₂,

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)_n-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine and
15 n is an integer of 0 to 20);

o, m, p-XCH₂-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine, n is
20 an integer of 1 to 20, and m is an integer of 0 to 20);

o, m, p-XCH₂-C₆H₄-O-(CH₂)_n-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)_n-CH=CH₂,

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)_n-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine and
25 n is an integer of 0 to 20);

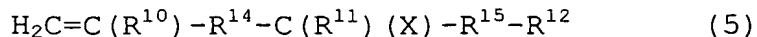
o, m, p-XCH₂-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine, n is
30 an integer of 1 to 20 and m is an integer of 0 to 20).

As the alkenyl-containing organic halide, there may further be mentioned compounds represented by the general formula 5:



35 (wherein R¹⁰, R¹¹, R¹², R¹⁴ and X are defined above and R¹⁵ is a

direct bond, $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group).

R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain one or more ether bonds) and, when it is a direct bond, the vinyl group is bound to the carbon to which the halogen is bound, to form an allyl halide. In this case, the carbon-halogen bond is activated by the neighboring vinyl group, so that it is not always necessary for R^{15} to be a $C(O)O$ group or a phenylene group, for instance, but it may be a direct bond. When R^{14} is not a direct bond, R^{15} is preferably a $C(O)O$ group, $C(O)$ group or phenylene group so that the carbon-halogen bond may be activated.

[0036]

As a specific example of compounds represented by the general formula 5, there can be mentioned,

$CH_2=CHCH_2X$, $CH_2=C(CH_3)CH_2X$,
 $CH_2=CHC(H)(X)CH_3$, $CH_2=C(CH_3)C(H)(X)CH_3$,
 $CH_2=CHC(X)(CH_3)_2$, $CH_2=CHC(H)(X)C_2H_5$,
 $CH_2=CHC(H)(X)CH(CH_3)_2$,
 $CH_2=CHC(H)(X)C_6H_5$, $CH_2=CHC(H)(X)CH_2C_6H_5$,
 $CH_2=CHCH_2C(H)(X)-CO_2R$,
 $CH_2=CH(CH_2)_2C(H)(X)-CO_2R$,
 $CH_2=CH(CH_2)_3C(H)(X)-CO_2R$,
 $CH_2=CH(CH_2)_8C(H)(X)-CO_2R$,
 $CH_2=CHCH_2C(H)(X)-C_6H_5$,
 $CH_2=CH(CH_2)_2C(H)(X)-C_6H_5$,
 $CH_2=CH(CH_2)_3C(H)(X)-C_6H_5$,

(in the above formulas, X is chlorine, bromine or iodine, and R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms). Among these, allyl chloride and allyl bromide are preferred from cost and availability viewpoint.

[0037]

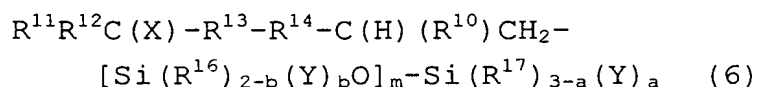
Specific examples of the alkenyl-containing sulfonyl halide are as follows:

o-, m- or p-CH₂=CH-(CH₂)_n-C₆H₄-SO₂X and
 o-, m- or p-CH₂=CH-(CH₂)_n-O-C₆H₄-SO₂X
 (wherein, in each formula, X is chlorine, bromine or iodine and
 n is an integer of 0 to 20), among others.

5 [0038]

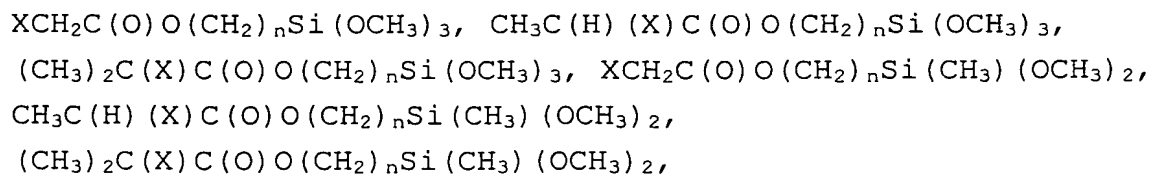
When an alkenyl-containing initiator is used, care should
 be taken since there is a possibility that olefin of the
 initiator may also react with the polymerization terminus.

The crosslinking silyl-containing organic halide is not
 10 particularly restricted but includes, among others, those
 having a structure shown by the general formula 6:

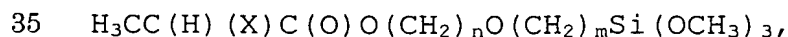
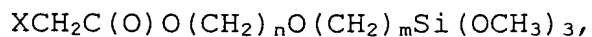


(wherein R¹⁰, R¹¹, R¹², R¹³, R¹⁴ and X are as defined above, R¹⁶
 15 and R¹⁷ each is an alkyl group having 1 to 20 carbon atoms, an
 aryl group having 6 to 20 carbon atoms, or an aralkyl group having
 7 to 20 carbon atoms, or a triorganosiloxy group represented
 by (R')₃SiO- (in which R' is a monovalent hydrocarbon group
 having 1 to 20 carbon atoms and the three R' groups may be the
 20 same or different) and, when there are two or more R¹⁶ and/or
 R¹⁷ groups, they may be the same or different, Y represents a
 hydroxyl group or a hydrolyzable group and, when there are two
 or more Y groups, they may be the same or different, a represents
 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0
 25 to 19, provided that the relation a + mb ≥ 1 should be satisfied.

As a specific example of compounds represented by the
 general formula 6, there can be mentioned,

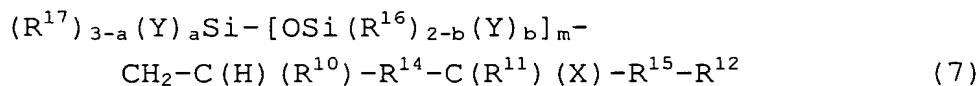


(wherein, in each formula, X is chlorine, bromine or iodine and
 n is an integer of 0 to 20),



- $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$
 $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 $\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 5 $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$
 (wherein, in each formula, X is chlorine, bromine or iodine,
 n is an integer of 0 to 20, and m is an integer of 0 to 20),
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 10 $\text{o,m,p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 15 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 20 $\text{o,m,p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-XCH}_2\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{o,m,p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 (wherein, in each formula, X is chlorine, bromine or iodine).

- 25 As further examples of the crosslinking silyl-containing
 organic halide, there may be mentioned those having a structure
 represented by the general formula 7:



- 30 (wherein R^{10} , R^{11} , R^{12} , R^{14} , R^{15} , R^{16} , R^{17} , a, b, m, X and Y are
 as defined above).

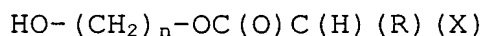
As a specific example of such compounds, there can be mentioned;

- $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}_6\text{H}_5,$ $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}_6\text{H}_5,$
 35 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})\text{-CO}_2\text{R},$ $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})\text{-CO}_2\text{R},$

$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_9\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_9\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
5 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$, $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
 (wherein, in each formula, X is chlorine, bromine or iodine, R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms.), and the like.

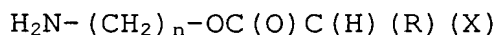
10 [0039]

The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



15 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

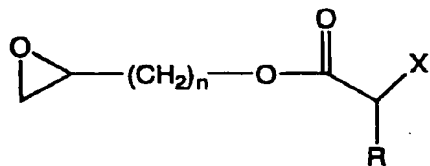


25 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The epoxy-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

30 [0040]

[Chemical 4]



5 [0041]

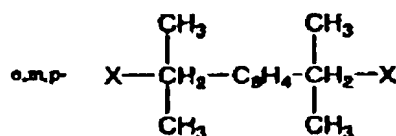
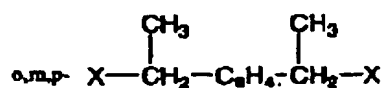
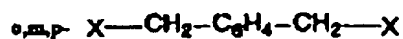
(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

10 An organic halide or sulfonyl halide having two or more initiation sites is used as an initiator. Specific examples are:

[0042]

[Chemical 5]

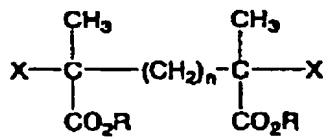
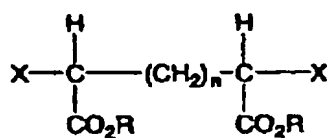
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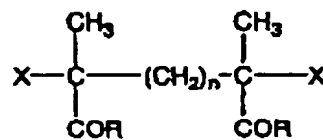
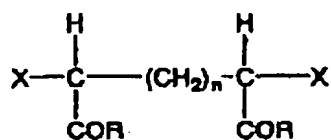
20

(in which C_6H_4 represents a phenylene group and X is chlorine, bromine or iodine);

25

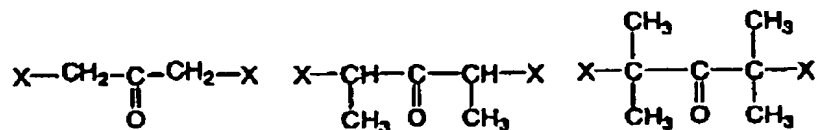


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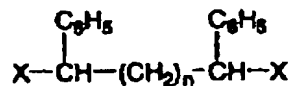


(in which R is an alkyl group having 1 to 20 carbon atoms, aryl or aralkyl group, n is an integer of 0 to 20 and X is chlorine, bromine or iodine);

35



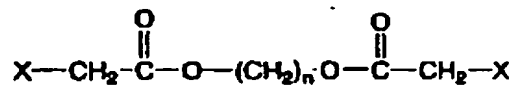
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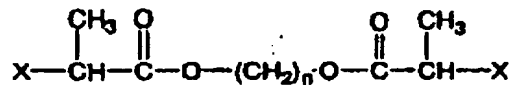
(in which X is chlorine, bromine or iodine and n is an integer of 0 to 20);

10 [0043]

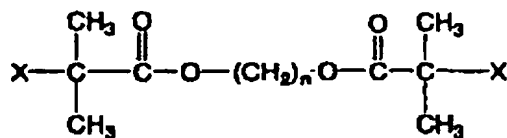
[Chemical 6]



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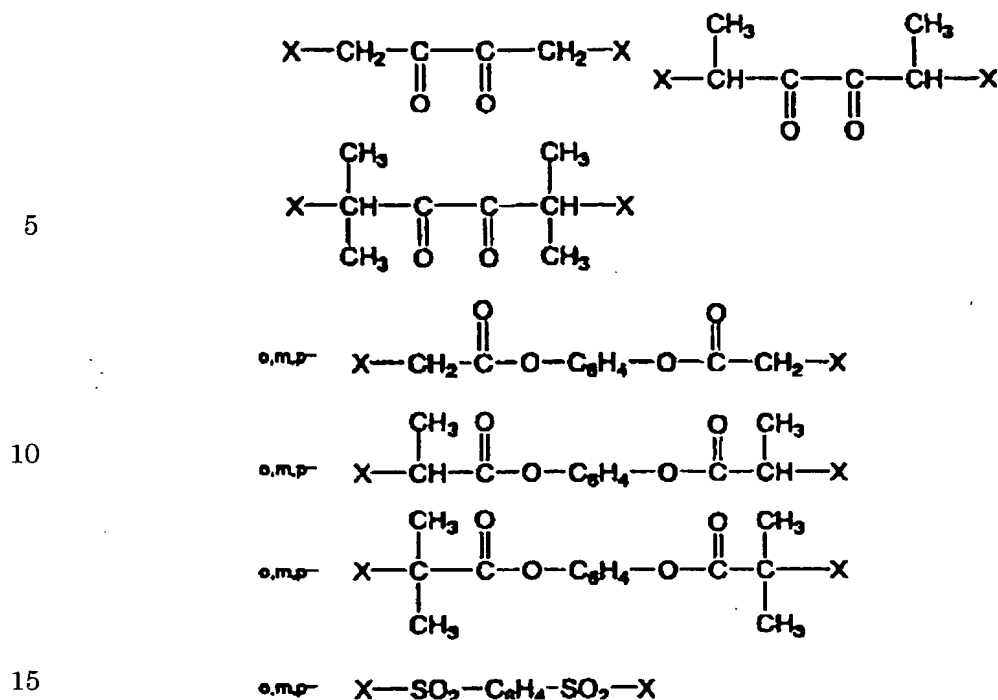


(in which n is an integer of 0 to 20 and X is chlorine, bromine or iodine);

25

30

35



(in which X is chlorine, bromine or iodine), and the like.
[0044]

<Catalyst of atom radical polymerization>

The transition metal complex to be used as a polymerization catalyst for the atom transfer radical polymerization is not particularly restricted but preferably is a metal complex containing an element of the group 7, 8, 9, 10 or 11 of the periodic table as a central metal, and more preferably are complexes of monovalent copper, copper (valence: zero), divalent ruthenium, divalent iron or divalent nickel. Among them, copper complexes are preferred in view of cost and reaction controllability. Specific examples of monovalent copper compounds are cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, cuprous perchlorate and the like. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof or a polyamine such as tetramethylethylenetriamine (TMEDA), pentamethyldiethylenetriamine or hexamethyl

(2-aminoethyl) amine, is added to enhance the catalytic activity. A tris(triphenylphosphine) complex of divalent ruthenium chloride ($\text{RuCl}_2(\text{PPh}_3)_3$) is also suited for use as a catalyst. When a ruthenium compound is used as a catalyst, an aluminum alkoxide is added as an activator. Furthermore, a bistris(triphenylphosphine) complex of divalent iron ($\text{FeCl}_2(\text{PPh}_3)_2$), a bistris(triphenylphosphine) complex of divalent nickel ($\text{NiCl}_2(\text{PPh}_3)_2$) and a bis(tributylphosphine) complex of divalent nickel ($\text{NiBr}_2(\text{PBu}_3)_2$) are also suited as catalysts.

10 <Solvent and temperature of living radical polymerization>

The above-mentioned living radical polymerization, and further atom transfer radical polymerization can be carried out in the absence or presence of various solvents. As the solvent, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; and carbonate solvents such as ethylene carbonate and propylene carbonate. These may be used singly or two or more of them may be used in admixture. The above polymerization can be conducted within the temperature range of room temperature to 200°C, preferably 50°C to 150°C.

<Addition of polymer (I)>

The time for adding the polymer (I) to the living radical polymerization system is not particularly restricted but is preferably in the terminal stage of polymerization. The amount of the polymer (I) to be added is not particularly restricted but is preferably such that the number of growing termini in living radical polymerization be equal to the number of the terminus represented by the general formula 1 in polymer (I).

[0045]

The polymer (I) may be added as such or in the form of a solution in a solvent which will not adversely affect the living radical polymerization.

5 Structure of the block copolymer

The structure of the block copolymer of the present invention is not particularly restricted but includes those copolymers classifiable on the basis of polymer (I) and of the system to which the polymer (I) is added, namely living radical
10 polymerization, as follows:

(1) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per molecule and a unifunctional initiator; (2) living radical polymerization using a polymer (I) having one group represented
15 by the general formula 1 per molecule and a bifunctional initiator; (3) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per molecule and a polyfunctional initiator; (4) living radical polymerization using a polymer (I) having two groups
20 represented by the general formula 1 per molecule and a unifunctional initiator; (5) living radical polymerization using a polymer (I) having more than two groups represented by the general formula 1 per molecule and a unifunctional initiator; (6) living radical polymerization using a polymer
25 (I) having two groups represented by the general formula 1 per molecule and a bifunctional initiator; (7) the case in which either of the number of the group represented by the general formula 1 and the number of initiation sites of the initiator in living radical polymerization is not less than 2 and the other
30 is not less than 3; and so forth.

In the case of (1), an AB type block copolymer is obtained; in the case of (2) or (4), an ABA type block copolymer is obtained; in the case of (3) or (5), a stellar block copolymer is obtained; in the case of (6), a multiblock copolymer is
35 obtained; and in the case of (7), a crosslinked block copolymer

is obtained.

[0046]

For each polymer block, various species can be synthesized. In an ABA type block copolymer, for instance, when
5 A is a polymer having a higher glass transition point (not specifically restricted but, for example, not lower than 25°C) and B is a polymer having a lower glass transition point (not specifically restricted but, for example, not higher than 25°C), properties as a thermoplastic elastomer can be expected. In
10 the case of stellar polymers as well, properties as a thermoplastic elastomer can be expected when a polymer block having a higher glass transition point is used as the exterior block and a polymer block having a lower glass transition point as the inside block.

15 [0047]

Accordingly, by the present invention, block copolymers in which various species of blocks are combined in various orders can be obtained, and can be used in various fields such as thermoplastic elastomers and impact resistance improving
20 agents.

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the block copolymer of the present invention is not particularly
25 restricted but is preferably less than 1.8, more preferably not more than 1.7, still more preferably not more than 1.6, much more preferably not more than 1.5, in particular not more than 1.4, most preferably not more than 1.3. In the practice of the present invention, the number average molecular weight can be
30 determined by GPC generally using chloroform as mobile phase and a polystyrene gel column and thus it can be expressed in terms of polystyrene equivalent.

Uses

<Thermoplastic elastomer>

35 The block copolymer obtained by the production method of

the present invention can be used in substantially the same fields of application as the existing thermoplastic elastomers. More specifically, it can be used for modifying resins or asphalt, for preparing compounds of the block copolymer with
5 resins (with a plasticizer, a filler, a stabilizer, etc. added as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be mentioned automotive upholstery and
10 exterior, electric and electronic fields, food wrapping films and tubes, drug containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

While the block copolymer obtained by the production
15 method of the present invention by itself can serve as a molding material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a high level of impact resistance when admixed with said resins.
20 Further, it can also be used as a processability improving agent, compatibilizing agent, flatting agent, heat resistance modifier or the like. Furthermore, improvement of gas barrier property based on an isobutylene polymer can be expected.
[0048]

25 The thermoplastic resins which can be improved in shock resistance by addition of the block copolymer of the present invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins,
30 polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic alkenyl compounds, vinyl cyanide compounds and (meth)acrylic
35 acid esters and 0 to 30% by weight of another vinyl monomer

copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene ether resins, polystyrene-polyphenylene ether resin blends and the like. Said block copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and polyester resins, among others, are preferred since they can readily show its characteristics such as improved weathering resistance and impact resistance.

[0049]

As the method of adding the block copolymer of the present invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an ordinary injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0050]

Furthermore, in the resulting resin compositions, there may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), acrylic graft copolymers and acrylic-silicone composite rubber type graft copolymers; stabilizers such as triphenyl phosphite; lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire retardants, e.g. decabromobiphenyl, decabromodiphenyl ether, and antimony trioxide; pigments such as titanium oxide, zinc

sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0051]

[Examples]

5 In the following, specific examples of the present invention are described. The following examples, however, are by no means limitative of the scope of the present invention. In the GPC measurement in Examples, a polystyrene gel column was used while using chloroform as mobile phase, and the values
10 of the molecular weight was expressed in terms of polystyrene equivalent.

(Production Example 1)

 A one-liter pressure glass autoclave was equipped with a stirring blade, a three-way cock and a vacuum line and, while
15 evacuating through the vacuum line, the polymerization vessel was dried by heating at 100°C for 1 hour. After cooling to room temperature, the three-way cock was opened to introduce nitrogen into the vessel to ordinary pressure.

[0052]

20 Then, while feeding nitrogen through one route of the three-way cock, a mixed solvent (155 mL of methylene chloride and 348 mL of n-hexane) dried by molecular sieve treatment was introduced into the autoclave using a syringe. Then, a solution of 7.5 mmol of DCC (compound A illustrated below) in 10 mL of
25 methylene chloride was added, followed by addition of 3.0 mmol of the additive α -picoline.

[0053]

 Then, a pressure glass liquefied gas sampling tube equipped with a needle valve and containing 112.8 g of
30 isobutylene dehydrated by passing through a column packed with barium oxide was connected with the three-way cock. The polymerization vessel proper was immersed in a dry ice-acetone bath at -70°C and cooled for 1 hour while stirring the vessel inside. After this cooling, the inside pressure was reduced
35 through the vacuum line and, then, the needle valve was opened

to introduce isobutylene from the pressure glass liquefied gas sampling tube into the polymerization vessel. Thereafter, ordinary pressure was restored by feeding nitrogen through one route of the three-way cock, the cooling was further continued for 1 hour with stirring, and the polymerization vessel inside

[0054]

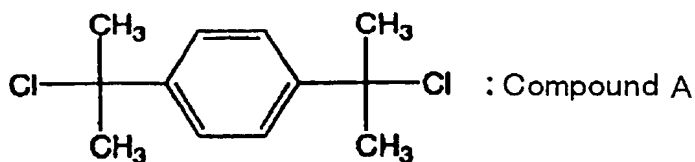
Then, polymerization was initiated by adding 4.1 mL (37.5 mmol) of TiCl_4 through the three-way cock using a syringe to initiate the polymerization and, after the lapse of 1 hour, 27.7 mL (150 mmol) of 1,9-decadiene was added. After further 8 hours of reaction, the reaction mixture was poured into water to thereby deactivate the catalyst. Then, the organic layer was washed with three portions of pure water. After phase separation, the methylene chloride, n-hexane and 1,9-decadiene were distilled off under reduced pressure to give an allyl-terminated isobutylene polymer.

[0055]

The structure of compound A is as shown below.

[0056]

[Chemical 7]



[0057]

Production Example 2

A 3-liter pressure glass autoclave was equipped with a stirring blade, a three-way cock and a vacuum line and, while evacuating through the vacuum line, the polymerization vessel was dried by heating at 100°C for 1 hour. After cooling to room temperature, the three-way cock was opened to introduce nitrogen into the vessel to ordinary pressure.

[0058]

Then, while feeding nitrogen through one route of the three-way cock, a mixed solvent (618 mL of methylene chloride and 1,001 mL of n-hexane) dried by molecular sieve treatment was introduced into the autoclave using a syringe. Then, a solution of 15 mmol of DCC (compound A illustrated below) in 50 mL of methylene chloride was added, followed by addition of 6.0 mmol of the additive α -picoline.

[0059]

Then, a pressure glass liquefied gas sampling tube equipped with a needle valve and containing 224 g of isobutylene dehydrated by passing through a column packed with barium oxide was connected with the three-way cock. The polymerization vessel proper was immersed in a dry ice-acetone bath at -70°C and cooled for 1 hour while stirring the vessel inside. After this cooling, the inside pressure was reduced through the vacuum line and, then, the needle valve was opened to introduce isobutylene from the pressure glass liquefied gas sampling tube into the polymerization vessel. Thereafter, ordinary pressure was restored by feeding nitrogen through one route of the three-way cock, the cooling was further continued for 1 hour with stirring, and the polymerization vessel inside temperature was raised to -70°C .

[0060]

Then, polymerization was initiated by adding 8.2 mL (75 mmol) of TiCl_4 through the three-way cock using a syringe and, after the lapse of 1 hour, 14.3 mL (90 mmol) of allyltrimethylsilane was added. After further 1 hour of reaction, the reaction mixture was poured into methanol to thereby terminate the reaction. The reaction mixture was stirred for a while and then allowed to stand to cause precipitation of the polymer.

[0061]

The thus-obtained polymer was again dissolved in n-hexane, the solution was washed with three portions of pure water and the solvent was then distilled off to give an allyl-terminated

isobutylene-based polymer.

For the polymers obtained in Production Examples 1 and 2, the percent yields were calculated based on the yields, the Mn and Mw/Mn values were determined by the GPC method, and the terminal structures were established by measuring, by the ¹H-NMR method, and comparing the intensities of the resonance signals of protons ascribable to the respective structures (initiator-derived proton: 6.5 to 7.5 ppm and polymer terminal vinyl proton: 4.5 to 5.9 ppm). The results are shown in Table 1.

[0062]

[Table 1]

Production Example	Yield (%)	GPC		NMR FN*
		Mn	Mw/Mn	
1	96	18700	1.45	1.78
2	100	9100	1.29	1.96

FN* : number of vinyl groups per molecule.

[0063]

[Effect of the Invention]

By adding, according to the present invention, alkenyl-terminated polymers produced by living cationic polymerization to a polymerization system for living radical polymerization, it is possible to obtain, with ease, block copolymers resulting from binding of these polymers to one another. Furthermore, since the production of the polymer to be added and the polymerization for adding thereof is the living polymerization, block copolymers well controlled in the structure can be obtained.

[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its subject to provide a method of easily producing a block copolymer composed of various living cationic polymerization polymers and a living radical polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] In the present invention, a block copolymer can be produced easily by adding a polymer (I) produced by living cationic polymerization and containing an alkenyl group in at least one terminus to a living radical polymerization system. Furthermore, the block copolymer and the polymer block of the present invention have a characteristic for being well controlled in the molecular weight.

[Selective Figure] none